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MANAGEMENT OF METAL-FINISHING SLUDGE

This publication (SW-561) was prepared by
E. P. CRUMPLER, JR.

U.S. ENVIRONMENTAL PROTECTION AGENCY

1977

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ABSTRACT

The disposal of metal-bearing sludges from treatment of metal finishing wastewaters is causing increased concern. Implementation of metal precipitation as the best available technology to meet effluent guidelines will increase the amounts of sludge requiring disposal. This report discusses the state-of-the-art of technology which can potentially manage the sludge. Disposal techniques, recycle and waste reduction technology are reviewed. The major advantages and disadvantages of each technique are presented. Current EPA research and demonstration efforts are also discussed.

The Metal Finishing Industry

Metal finishing operations are found throughout the primary metal and metal fabrication industries. The metal finishing process contains any or all of the following operations:

1. Cleaning and pickling
2. Buffing and polishing
3. Electroplating
4. Immersion plating (metal deposit by chemical exchange)
5. Phosphating and oxidizing
6. Painting
7. Electropainting
8. Anodizing
9. Annealing and case hardening

The metal finishing industry consists of two types of shops: captive and job. A captive shop is a part of a larger manufacturing operation requiring metal finished parts. The automobile industry is an example. A job shop performs contract metal finishing on parts owned by its customers. Its sole business is metal finishing. The technology discussed in this report applies to both captive and job shops.

Sources of Waste

Metal finishing operations are batch operations. The parts to be treated are immersed in a chemical bath where one step in the finishing process takes place. After the treatment is completed, the part is removed and the process solution is rinsed off before the next step. An example of a typical metal finishing line is the plating of an automobile bumper. The basic steel bumper passes through the following steps:

1. Solvent cleaning
2. Acid cleaning
3. Zinc plating
4. Copper plating
5. Nickel plating
6. Chromium plating

After each step, the bumper is rinsed with water to remove the process solution. The rinse minimizes contamination of the subsequent process solutions as well as maintaining a quality finish. The large volume of contaminated rinse water containing dilute quantities of process solutions (dragout) is one source of waste.

A second source of waste is the dumping of spent process solutions. Process baths accumulate impurities during their use and bath additives deteriorate with time. In many cases, these baths cannot be satisfactorily reclaimed and require disposal. This is a major source of waste.

Other wastes in metal finishing shops come from process spills, tank leaks, and air pollution control systems. All of these wastes contain metals, acids, bases, organics and solvents in solution. To meet discharge water standards, treatment of some type is necessary to remove most of the pollutants.

1977 Effluent Guidelines

The 1977 Effluent Guidelines for the Electroplating Industry identify the Best Practical Control Technology Currently Available (BPCTCA). The waste treatment process produces a sludge high in metal content. The BPCTCA treatment process is described below:

a. The hexavalent chromium stream is segregated for chemical reduction to trivalent chromium. This reduction is most frequently accomplished by using sulfur dioxide gas. Other reducing agents may be used such as sodium bisulfate, ferrous sulfate, or sulfuric acid, but sulfur dioxide is preferred due to its lower cost. The chemical reduction is necessary since hexavalent chromium will not precipitate by pH adjustment.

b. The cyanide bearing streams are segregated for chemical destruction of the cyanide. The cyanide is oxidized by use of chlorine gas or sodium hypochlorite in an alkaline solution. The cyanide radical (CN+) is broken down into nitrogen and carbon dioxide which are vented as gases. Metal hydroxide solids are also formed during the destruction reaction due to the alkalinity of the solution.

c. The treated chromium and cyanide streams are combined with the remaining acid-alkali waste waters and pH is adjusted to the 7.0 to 9.5 range. The pH adjustment causes the metal ions to precipitate as hydrated metal oxides. Lime is the preferred pH adjustment reagent due to both lower cost and superior settling properties. The solubilities of most metals are at their minimum

in the pH range of 8.0 to 11.0 as illustrated in Figure 1. The water-sludge mixture passes into a clarifier where sludge thickening occurs. The decanted water is passed through a sand filter before discharge to receiving waters. The sludge, normally two to three percent solids, is usually disposed of in a lagoon, drying bed, or a landfill. In some cases, the sludge may be dewatered to reduce the amount of water to be handled. The damage potential inherent in disposal of the water treatment sludges involves resolubilizing of the metal hydroxides in water or leachate with pH's at or below 7.0. The solubility curve shown in Figure 1 indicates the rapid increase in metal solubility as the pH drops. Even rainwater at a pH value of 5.5 to 6.5 will accelerate resolubilization.

The metal content of a typical electroplating sludge is shown in Table 1. Eighty-five percent of the sludge, on a dry basis, is estimated to be metal hydroxides.

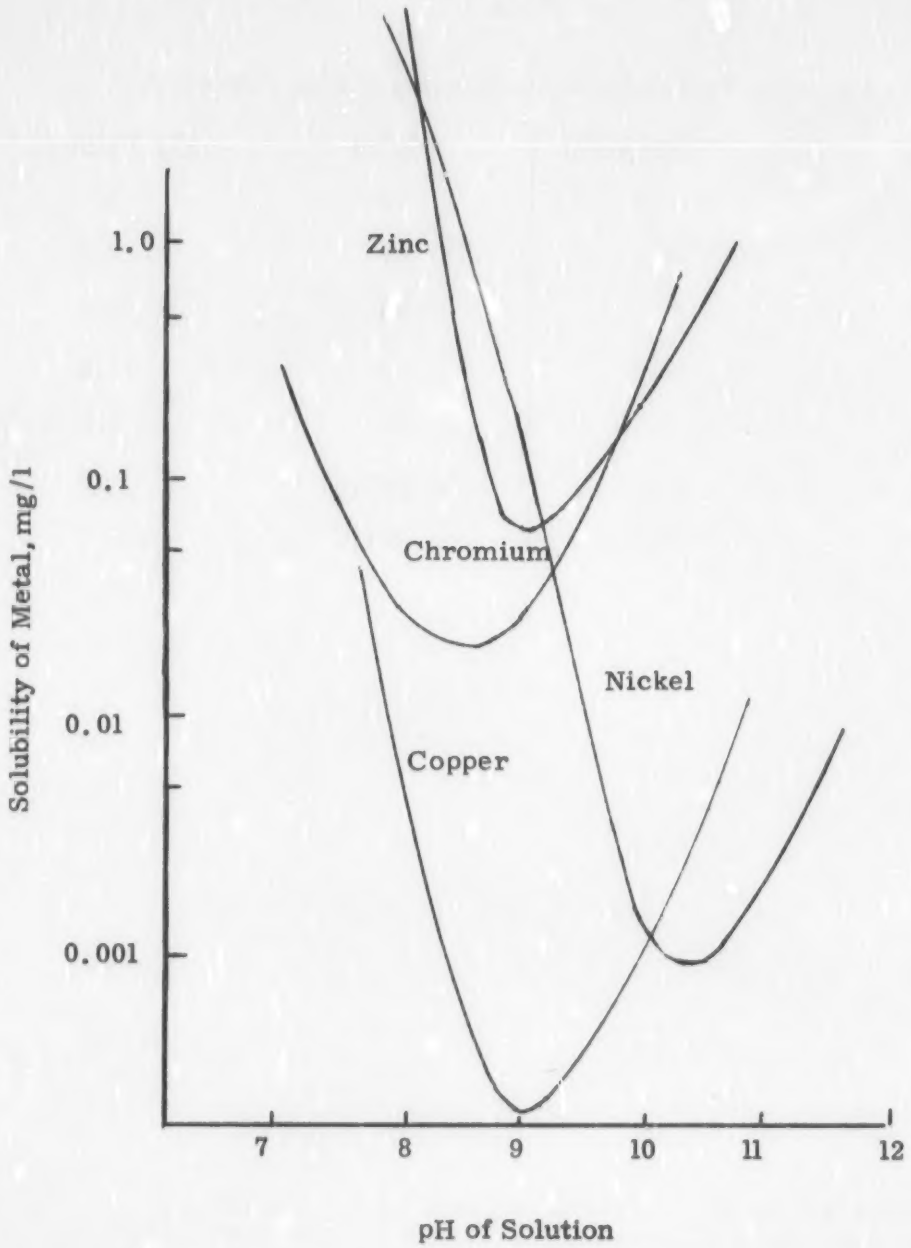
Estimated Quantities of Sludge

Battelle estimates that 19,792 metric tons (dry weight) of water treatment sludge were produced in 1975 from United States job shops. The 1977 estimate is 56,549 metric tons and the 1983 estimate is 74,080 metric tons (dry weight).[1] Although no estimate of the quantities of sludge produced by captive shops was made, the tonnage is expected to be much greater.

This quantity of metal-containing sludge presents a major environmental problem for disposal. Surface and groundwater will certainly be threatened by inadequate disposal.

This paper will attempt to review the significant technological alternatives potentially capable of addressing the wastewater sludge problem. It is part of the Hazardous Waste Management Division's mission to identify an economical technology for (1) disposing safely of these sludges, (2) recycling the wastes, or (3) eliminating the waste.

Figure 1. Solubility of Metal Hydroxides vs. pH*



*Development document for proposed effluent limitations guidelines and new source performance standards; copper, nickel, chromium, and zinc segment of the electroplating point source category. Washington, U.S. Environmental Agency, Office of Air and Water Programs, Effluent Guidelines Division, Aug. 1973. 206 p.

TABLE 1*

Estimated Aggregate Electroplating Sludge Composition

Compound	Dry Weight %	Metal	Dry Weight %
$Cu(OH)_2$	12.3	Cu	8.0
$Cr(OH)_3$	14.8	Cr	7.5
$Ni(OH)_3$	39.1	Ni	21.0
$Zn(OH)_2$	17.1	Zn	11.0
$Cd(OH)_2$	1.7	Cd	1.0
Impurities	15.0	Non-metals	51.5
Total	100.0	Total	100.0

*Hezir, J. S. Impacts of new water pollution regulations on solid waste management: New York City. Washington, U.S. Environmental Protection Agency, Office of Solid Waste Management Programs, Sept. 1973. 103 p. (Unpublished report.)

WASTE TECHNOLOGY REVIEW

For purposes of presentation, the various technologies can be grouped into five categories. Each category represents a specific approach to solving the metal hydroxide sludge disposal problem.

1. Disposal techniques which have the potential for environmentally adequate disposal of metal hydroxide sludges,

2. Processes that produce a modified metal containing sludge,

3. Internal recycle processes for recovery of chemicals removed in rinse water,

4. Recovery of metal from mixed metal hydroxide sludges, and

5. Recovery of metals from segregated solutions and sludges.

Detailed information on each process containing descriptions, known state-of-the-art, economics, and major advantages and disadvantages are presented.

Some processes which are being developed for electroplating waste treatment are not included in this assessment. Specifically, the following have not been addressed:

1. Cyanide destruction by ozone,

2. Cyanide destruction by electrolysis,

3. Hexavalent chromium reduction using iron, and

4. Waste-plus-waste techniques developed by the Bureau of Mines.

These processes, while having operational cost advantages over the 1977 BPCTCA, do not affect the composition or quantity of hydroxide sludge formed. These are only modified destruction methods, resulting in the same sludge.

In a similar manner, the various techniques to reduce rinse water consumption are not presented in this report. Rinse water reduction will affect the size of the wastewater treatment facilities and affect treatment economies, but the quantities of sludge produced are not reduced, since the dragout from the plating bath is not reduced. Techniques such as spray rinsing, reduced plating bath concentration, spill prevention controls, and improved housekeeping are not presented since these do not represent new technology. These are well developed process modification techniques which require minimal capital investment and can reduce sludge formation only to a certain degree.

A. Disposal Technology Potentially Environmentally Adequate

Four techniques have been identified as having the potential to dispose of electroplating wastewater sludge. These are:

1. Encapsulation
2. Heat Treatment
3. Chemical Lining of Disposal Cells
4. Chemical Fixation

Individual summaries follow.

ENCAPSULATION

Description

Encapsulation of a waste involves packaging and containment of a specific quantity of a hazardous waste to prevent leaching. The technique can range from disposal in sealed concrete crypts or missile silos to the two-stage process being developed by TRW System Inc., under EPA contract.[2,3] The TRW process incorporates the waste into a solid inner matrix to reduce the solubility and the surface area available for dissolution. The solid matrix is then coated with an impervious encapsulation medium. The encapsulation medium waterproofs the inner matrix and protects it from external physical and chemical attack after disposal. It should be noted that the current practice of burying waste material in steel drums, without further encapsulation is not adequate, since the steel is readily corroded, releasing the hazardous contents.

State-of-the-Art

Hazardous Wastes are being disposed of in concrete underground missile silos in Idaho which are expected to be environmentally sound. However, this technique is dependent on the availability of abandoned underground military installations and is, therefore, not a generally usable disposal method. Several Mississippi disposal sites are using sealed concrete culvert pipe to dispose of pesticide containers and residues.[2] However, this technique is considered a temporary method until a more permanent disposal method can be devised.

The TRW work being sponsored by the Solid and Hazardous Waste Research Division, Cincinnati, is currently examining a series of organic polymers as encapsulating materials. Polybutadiene resins are being tested as inner matrices, and polyvinylchloride plastisols, epoxies and polyethylene resins are being evaluated for use as outer encapsulation media. The materials have been tested in bench-scale studies and results have been promising. Current activities are encapsulation of actual industrial wastes and testing under varied environmental conditions.

Economics

TRW has estimated the cost of the organic resin encapsulation process to be $85.10 per ton of dry waste.[3] Work now underway is focused on reduction of costs by the use of waste polymers. The hoped-for reduction in cost is expected to bring the unit cost down to approximately $40/ton.[3]

Advantages

1. Encapsulation may be the only usable method for ultimate disposal of environmentally persistent toxic elements such as arsenic.

Disadvantages

1. Encapsulation in concrete pipe or crypts may not be an environmentally sound practice.
2. The TRW technique appears to be expensive and complex.
3. Land disposal is still required.
4. No resource recovery is practiced.

HEAT TREATING OF SLUDGE

Description

High temperature heat treatment is capable of reducing the solubility of metal finishing sludge, rendering the sludge potentially safe for land disposal. The sludge could be heated to a temperature where the metal hydroxide would thermally convert to metal oxides. The oxides of metals tend to be much less water soluble than their hydroxides. The sludge would take on the form of a slag with a reduced volume, and should present less of an environmental hazard after disposal.

State-of-the-Art

Laboratory work to determine the conditions required to convert the metal hydroxides to metal oxides has been done in Zurich, Switzerland, by Dr. R. Braun of EAWAG.[4] Actual plating sludges were subjected to controlled temperature conditions followed by water solubility tests. A plot of the temperature-solubility relationship for an actual plating shop sludge is shown in Figure 2. From his laboratory work, Dr. Braun concluded:

1. 1,100 to 1,200 C temperatures are required to achieve chemically stable, water insoluble structures.

2. Treatment of metallic sludges in conventional incinerators at 800 to 1000 C is inadequate to achieve sufficient reduction in water solubility.

Economics

From the laboratory work, Dr. Braun concluded that a full-scale heat treatment process would be expensive although no cost estimates are given.

Advantages

1. The solubility of the metals is greatly reduced by converting to metal oxides, thus reducing the potential leachability.

2. The volume of the sludge is reduced by drying.

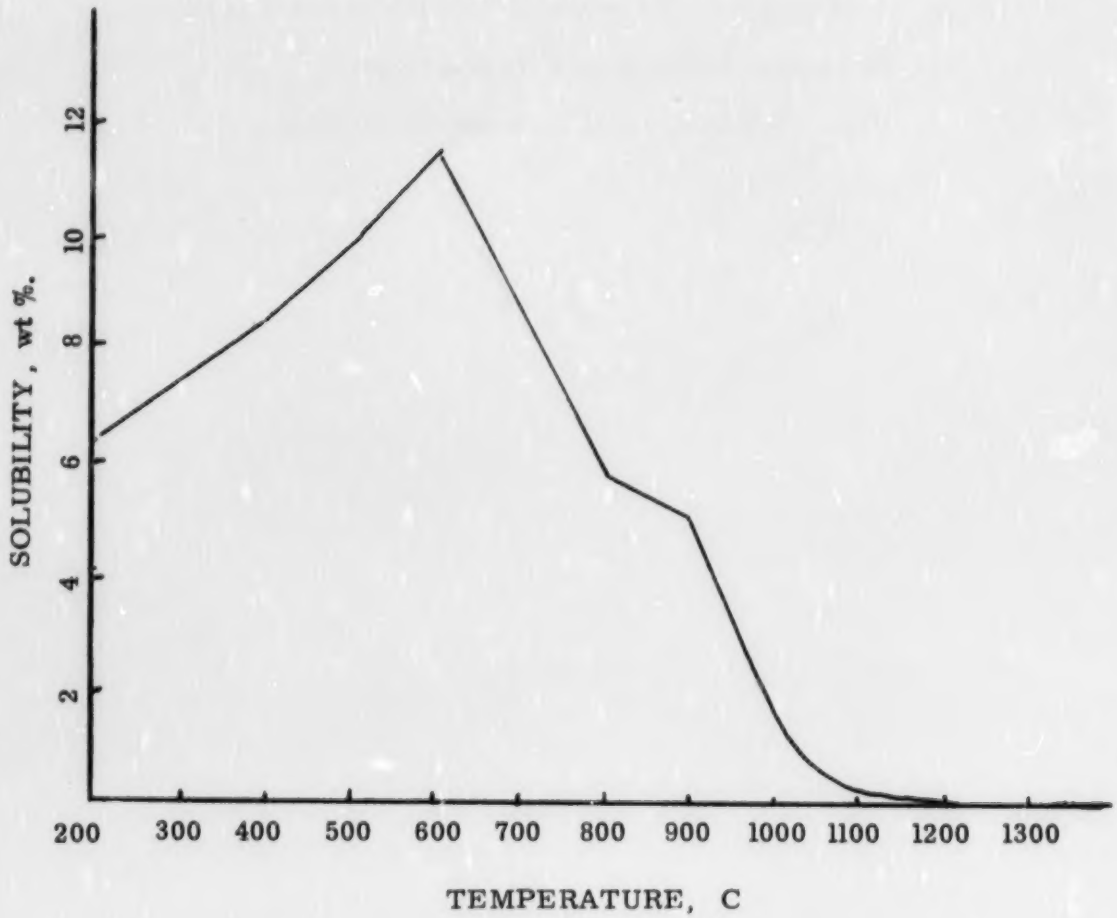


Figure 2 Water Solubility of a Heat Treated Plating Sludge.*

*Braun, R. Problems in the removal of inorganic industrial slurries. In Wastes: solids, liquids and gases. ACHEMA Symposium, 1970, Frankfurt. New York, Chemical Publishing Company, Inc., 1974. p. 203.

Disadvantages

1. The cost to heat treat sludges is expected to be expensive.

2. Land disposal of the treated sludge is still required.

3. No recovery of resources is practiced.

4. Heat treating appears to be energy intensive.

CHEMICAL CONTAINMENT

Description

One potential environmentally adequate method to dispose of electroplating wastewater sludge involves surrounding the sludge with a medium which will ensure alkalinity of any liquids coming into contact with the sludge. The object is to keep the pH of any leachate within a range of 7.0 to 10.0 to minimize the metal solubility. By maintaining this pH range, the rate of release of the metals is lowered to a level which will not impact the groundwater significantly.[5] This technique cannot provide total containment of the sludge since the metal hydroxides cannot be maintained totally insoluble by pH adjustment.

To illustrate the technique, a sketch of a disposal method currently being used at the Armstrong Cork Company Carpet plant near Lancaster, Pennsylvania, is shown in Figure 3. The Carpet Plant accumulates a heavy metal sludge mixed with rubber latex in storage tanks at the plant site until sufficient quantity is obtained to fill a sludge cell. A trench is opened about every six months, lined with a minimum of three inches of limestone and the sludge mixed with fly ash or soil is dumped into the trench. The sludge is immediately covered with soil and contoured to minimize percolation of runoff through the trench.

State-of-the-Art

The site at Lancaster, Pennsylvania, has been in operation since March 1971. Quarterly testing of the groundwater at the site has revealed no increase in heavy metals. The company has been unable to obtain any samples to date from test lysimeters buried under two of the beds. The Pennsylvania Department of Environmental Resources is requiring the separate landfilling of heavy metal sludge using the limestone envelope for all new landfill permits.[6]

Economics

No data are available on the increase in land disposal cost due to use of this technique. Cost data are needed.

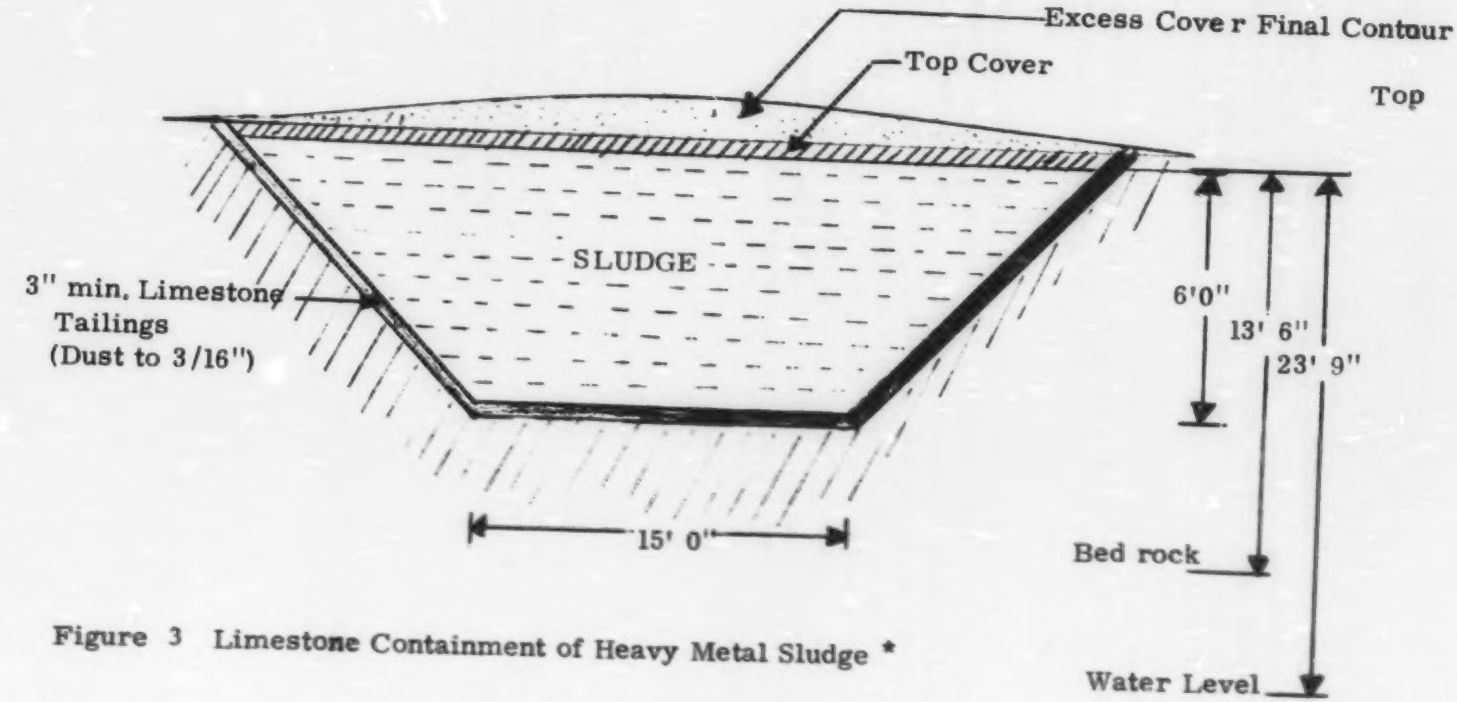


Figure 3 Limestone Containment of Heavy Metal Sludge *

*Drawing no. MR-A-12, Lancaster, Pa., Armstrong Cork Company, Central Engineering Department, 1971.

Advantages

1. Limestone containment is a land disposal technique which can be applied in a very short time due to its simplicity.

2. Proper inventory of sludges being buried would allow for future recovery.

Disadvantages

1. This technique requires land for disposal.

2. The environmental adequacy has not been fully demonstrated.

CHEMICAL FIXATION

Description

Chemical fixation uses a physical-chemical matrix structure to tie up hazardous liquids and solids for disposal. The matrix structure prevents or retards leaching of the waste into the environment. A number of commercial fixation processes are available. These processes use materials such as cement, fly ash, and limestone with the addition of organic polymers or inorganic silicates to produce a friable, soil-like material. The fixation product may or may not be suitable for landfills or construction materials.

State-of-the-Art

A number of firms offer chemical fixation commercially. Some processors have portable equipment which can be used for on-site treatment at a customer's plant.[7] Units are also sold for permanent installation at sites requiring continuing processing of wastes.[8]

The significant gap in the state-of-the-art is the lack of supportable data which accurately identifies the effectiveness of the fixation, i.e., the leachability of the fixed product. A joint EPA-Army Corps of Engineers project to identify the pollution potential of a number of chemically fixed industrial wastes is being conducted at the U.S. Army Engineers Waterways Experiment Station, Vicksburg, Mississippi.[9] Ten industrial sludges, including an electroplating sludge are being fixed by seven different commercial fixation processes. A matrix of the sludge-fixation process combination being studied is shown in Table 2. Four of the seven processes will be used on the electroplating sludge chosen for the study.

Experimental work is being done both in the laboratory and in the field. The project is expected to be completed by June 1977. The environmental adequacy of chemical fixation of electroplating sludges will be known with more certainty after completion of the project.

TABLE 2

MATRIX OF SLUDGES AND PROCESSES

UNDER STUDY BY CORPS OF ENGINEERS, VICKSBURG, MISS.

Sludges	Chemfix	Lancy	NECO	IUCS	WEHRAN	Dravo	TRW
1. Flue gas desulfurization-lime scrubber-Eastern Coal	X	X		X	X	X	
2. Electroplating	X		X	X			X
3. Nickel-cadmium battery	X			X			
4. Flue gas desulfurization limestone scrubber-eastern coal	X	X		X	X		
5. Flue gas desulfurization-double alkali-eastern coal	X	X		X	X	X	
6. Flue gas desulfurization-limestone scrubber-western coal	X	X		X	X	X	
7. Pigment manufacturing			X				
8. Chlorine manufacturing sludge	X			X			
9. Flue gas desulfurization double alkali-western coal	X	X		X	X		
10. Calcium fluoride manufacturing	X			X			

Economics

The charges for fixation of industrial wastes will vary widely depending on a number of factors. Among the factors determining cost are the process selected, the character of the waste, whether equipment is purchased or provided periodically by the vendor, trucking charges, and landfilling costs. A typical price range quoted by several processors is $8.00 to $20.00 per metric ton of waste.[11, 12, 14] The disposal site for the fixation product is supplied by the waste generator.

Advantages

1. Chemical fixation is commercially available from several sources.
2. Applicable to both large and small sludge generators.
3. Cost of fixation is reasonable.
4. No capital is tied up other than land for disposal.
5. Wastes may be stabilized so that metal ions are not available (readily) to the environment.

Disadvantages

1. Environmental adequacy of fixation products not yet fully established, although the product is certainly environmentally superior to raw sludge.
2. Landfilling is still required.
3. No resource recovery is practiced.
4. Sludges must be pumpable to feed mixing and discharge equipment.

B. Water Treatment Process Producing a Nonhydroxide Sludge

Two wastewater treatment processes have been identified which produce a nonhydroxide metal sludge. These are:

1. Sulfide Precipitation

2. Starch Xanthate Precipitation

Individual process summaries follow.

SULFIDE PRECIPITATION

Description

The sulfides of many metallic ions have very low solubilities in water, usually much lower than the corresponding hydroxide. An example is nickel. Nickel hydroxide has a water solubility of 1.3×10^{-1} gm/l @ 18 C.[11] Nickel sulfide has a solubility of 3.6×10^{-2} gm/l @ 18 C.[11] The sulfide is only 27 percent as soluble as the hydroxide. A soluble sulfide such as ferrous sulfide is added to the wastewater at a pH range of 5 to 7. The heavy metals form sulfides which precipitate readily. The sludge formed is reported to be more dense than a corresponding hydroxide and easily dewatered to 50 percent solids with gravity filtration.[12]

The long-term stability of the sulfide sludge is not known. Speculation on the weathering of sulfide sludges indicates that sulfuric acid might be formed by oxidation and metal release would follow.[5]

State-of-the-Art

The process has been demonstrated on a pilot-scale. The number of installations, if any, is not known. The Industrial Waste Treatment Laboratory, Edison, New Jersey, has granted $30K to the Metal Finishers' Foundation to conduct a pilot plant investigation designed to optimize the process and evaluate economic feasibility of a novel sulfide precipitation process. This project is currently in the draft report stage. The Edison Lab intends to fund a full-scale demonstration in the near future.[12]

Economics

Exact data comparing the costs of hydroxide precipitation vs sulfide precipitation are not available. The Edison grant work will give detailed projections of costs.

Advantages

1. Sulfide Precipitation will give better water effluent quality than hydroxide precipitation.

2. Sulfide sludge is reportedly easier to dewater than hydroxide sludge.

Disadvantages

1. A sludge is formed which requires disposal.

2. No recovery of metals is practiced.

3. The long-term stability of the sludge under landfill conditions is unknown.

STARCH XANTHATE PRECIPITATION

Description

A process to effectively remove metal ions from solution has been developed at the Northern Regional Laboratory of the United States Department of Agriculture. An insoluble cross-linked xanthate compound derived from corn starch acts as an ion exchange resin to remove heavy metals in water. The starch xanthate is slurried with vigorous agitation into the metal bearing solution. A contact time as short as five minutes is sufficient to ensure removal. For example, a solution containing 31,7700ug/l (ppb) of copper was reduced to 22ug/l (ppb) of copper in five minutes.[13] The insoluble starch settles very rapidly once agitation is stopped. Residual heavy metal concentration in solutions treated are typically much lower than existing effluent guideline concentrations.

The metals are reported to be reclaimable from the starch solids by treatment with nitric acid. The starch can be reused, but must be processed to regenerate the active site cross-linking. The stability of the starch-metal complex under landfill conditions has not been studied but speculation seems to indicate that the organic structure would break down rapidly and release the metals to the environment.

State-of-the-Art

Starch xanthate treatment development is still in the laboratory stage. No full-scale applications are known. The Industrial Waste Treatment Laboratory, Edison, New Jersey, has granted $39K to the United States Department of Agriculture, Peoria, Illinois, to conduct a pilot plant evaluation. This project is expected to be completed by July 1976.

Economics

The United States Department of Agriculture estimates the cost to manufacture starch xanthate at $0.20 to $0.22 per pound.[13] The claimed high capacity to bind metals indicates that the starch process may provide significant savings over conventional destruction processes. The Edison grant work due July 1976 will provide additional cost projections.

Advantages

1. Initial cost estimates indicate a potential reduction in waste treatment costs.

2. Metal removal from the starch compound is efficient.

3. The technique may have potential for treatment of segregated metal streams and subsequent recovery of pure metals.

Disadvantages

1. The ion exchange reaction is non specific for metals in a mixed metal solution.

2. The sludge is probably unsuited for land disposal due to its organic nature.

C. Internal Recycle of Rinse Water Dragout

Seven processes which can recycle the plating metal dragout have been identified. These processes are in various stages of development ranging from bench-scale to widespread commercialization. These are:

1. Evaporative Recovery
2. Reverse Osmosis
3. Ion Exchange
4. Electrodialysis
5. Freeze Separation
6. Solvent Rinsing
7. Ion Flotation

EVAPORATIVE RECOVERY

Description

Evaporative recovery of processing chemicals from plating rinse waters is an established method for reducing electroplating effluents. Evaporative recovery concentrates rinse waters containing the dilute plating chemicals up to the concentration of the plating bath and returns this concentrated solution to the plating tank. The evaporated water is condensed and reused in the rinsing tanks. Figure 4 illustrates the principle of evaporative recovery in a closed loop counter current rinsing system. The closed loop system is capable of recovering for reuse in excess of 95 percent of the chemicals lost from dragout. No external rinse water is added except to replace losses to atmospheric evaporation and spills. The only chemicals supplied to the plating bath are those needed to replace what is actually deposited on parts and that lost by spillage.

In metal plating systems, dragout serves to purge baths of contaminants resulting from the processing operation. The buildup of impurities, which can cause serious quality problems in evaporative recovery operations, may be prevented by the incorporation of techniques such as ion exchange, filtration, precipitation, and activated carbon treatment.

The benefits of this type of operation are the elimination of contaminated rinse water discharges which reduces metal sludge formation in wastewater treatment, the recovery and reuse of processing chemicals, the reduction in water consumption for rinsing, and the production of a small amount of waste from the associated impurity purge system.

State-of-the-Art

Evaporative recovery is a fully developed technology with an estimated 200 to 300 installations in the United States.[14] EPA's Industrial Waste Treatment Research Laboratory at Edison, New Jersey, has a grant in progress to demonstrate Evaporative Recovery of chromium rinse waters at Advanced Plating Company, Cleveland, Ohio. This demonstration will establish the effectiveness and economics of treating chromic acid rinse waters with a new evaporator design expected to be attractive for small platers. The project report is expected in April 1976.

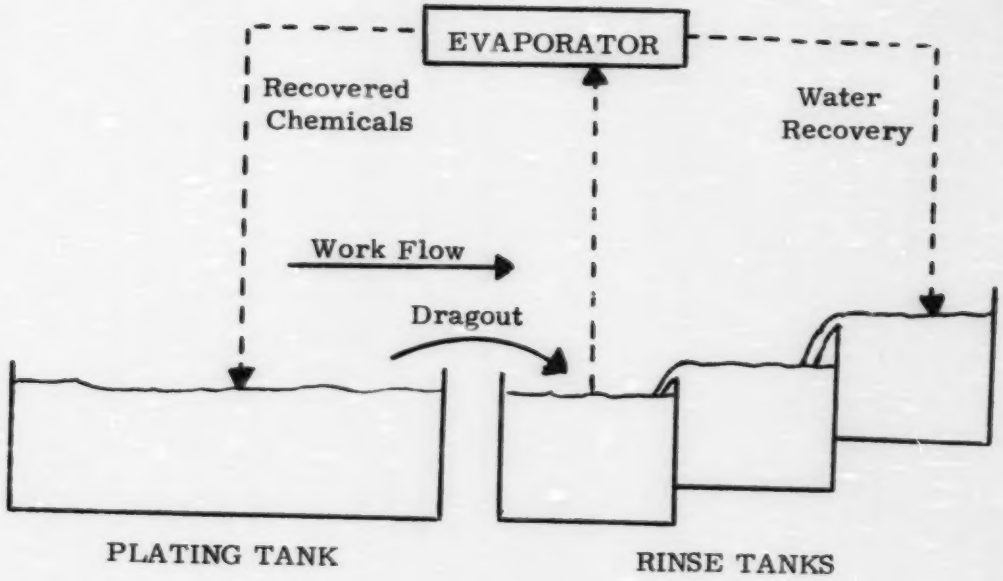


Figure 4 Closed-Loop Evaporative Recovery System

Economics

A typical evaporator unit costs $37K installed.[15] The operating cost of a unit sized to produce 10 gpm of distilled water for reuse will be approximately $2.50 per 1000 gal. of water distilled.[15] The savings in chemical cost will often offset the operating cost. One installation operating on a chromic acid bath has an annual operating cost of $9,301 per year but recovers $61,380 per year of chromic acid.[16] Adding an additional savings of $30,073 per year in reduced wastewater treatment cost, the net annual savings to the operation is $82,152.[16] Current economic data for an evaporative recovery system in a small plating shop will be available from the EPA/Advanced Plating Demonstration in April 1976.

Advantages

1. The loss of valuable chemicals is eliminated.

2. The water treatment sludge from treating the rinse water is eliminated. Treatment of a bleed stream is necessary to remove buildup impurities.

3. Water use in the rinsing operation is greatly reduced.

Disadvantages

1. Application to many plating baths is limited due to the buildup of degraded organic additives and heat sensitivity of some bath components.

2. Energy requirements are high where a waste heat source is not readily available.

3. Initial capital costs may be high for a small shop.

REVERSE OSMOSIS

Description

Reverse osmosis is a membrane technique which accomplishes pollution abatement by purifying the rinse water for reuse and concentrating the dragout chemicals for return to the plating bath. This technique is normally used in conjunction with counter current rinsing to minimize water volume. The system, when set up in a closed loop (see Figure 5), is designed to recover 95+ percent of the chemicals lost in the rinse water for reuse in the plating bath. No external rinse water is added except to replace evaporative and spill losses. Chemicals are added to the plating bath to replace only the chemicals actually plated onto parts plus any spills.

In reverse osmosis, pressure is used to force the water molecule through a membrane, while the larger plating chemical molecules are rejected and concentrated. The structure and durability of the membrane is the key to successful applications.[18] Use of a filter ahead of the membrane is required to prevent blinding of the membrane with solid particles. Impurity buildup in the closed system may be reduced by ion exchange, chemical precipitation and activated carbon.

This system impacts on sludge formation by reclaiming the plating chemicals and reducing water treatment sludge. Reduction in water consumption is an added benefit.

State-of-the-Art

The technology of reverse osmosis is in a relatively advanced state of development. Commercial units are available and electroplating rinse water recycle installations are operating with varying degrees of success. The lack of membrane materials capable of handling the wide pH and temperature range encountered in electroplating baths has hindered widespread use of reverse osmosis. New membranes are being developed with assistance from EPA. The Industrial Waste Treatment Research Laboratory at Edison has a development grant to investigate new membranes at Celanese Corp. Also, the Cincinnati Industrial Waste Treatment Research Laboratory has a pilot plant study grant to evaluate new membranes. In addition, Edison has two current demonstration grants to evaluate reverse osmosis on zinc cyanide plating rinse water and on nickel plating rinse water. Completion of the nickel recovery system demonstration was scheduled for April 1975 and the zinc cyanide demonstration for October 1975.

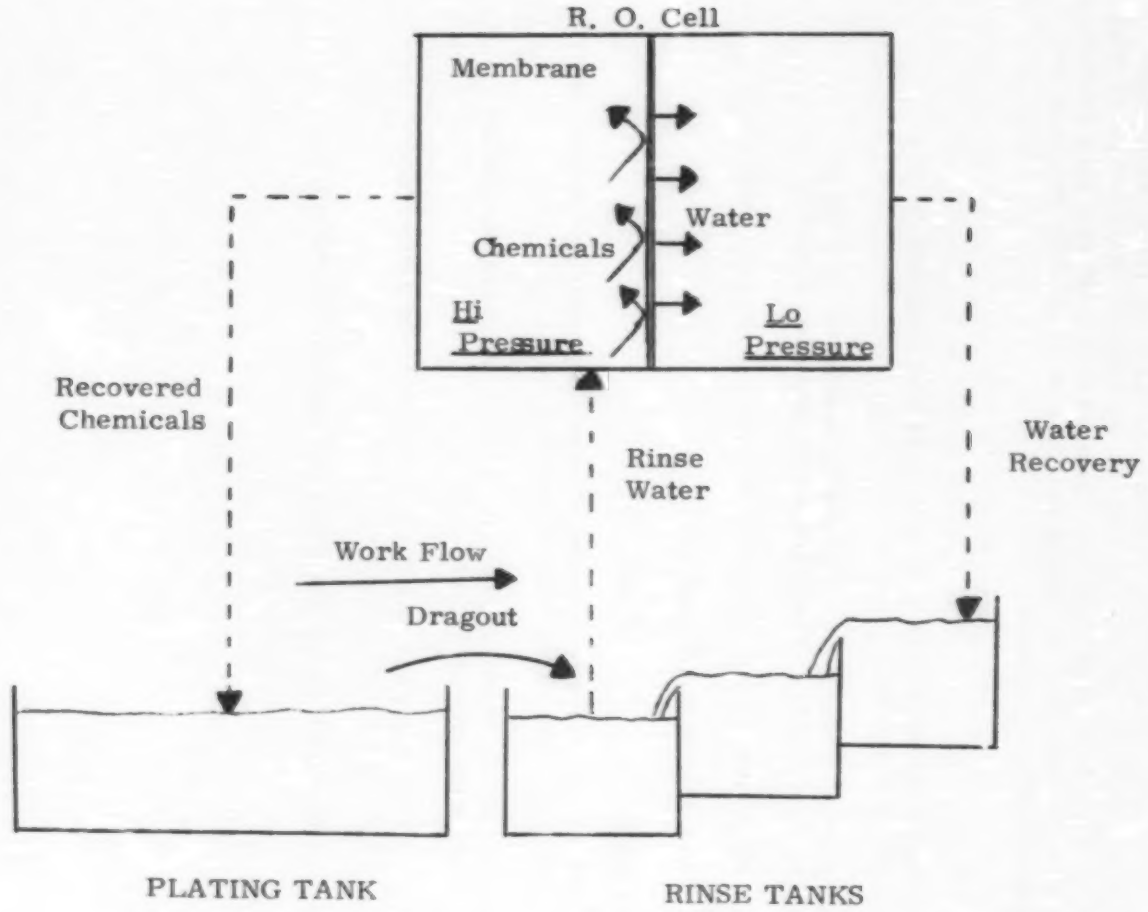


Figure 5 Closed-Loop Reverse Osmosis Recovery System

Economics

Capital and operating costs compared to evaporation are relatively low for reverse osmosis technology. One installation returning 500 gal. per day of concentrated nickel sulfate solution to the plating bath cost $10K to install and $13 per day to operate.[19] A recovery of $548 per day of nickel sulfate from the rinse waters produces very favorable economics. Current data on economics will be available from the two EPA sponsored demonstrations.

Advantages

1. Valuable chemicals are recovered and recycled to the plating process.

2. Sludge formation at wastewater treatment is reduced or eliminated. Treatment costs are also reduced.

3. Water use in the rinsing operation is greatly reduced.

4. Energy consumption is low.

Disadvantages

1. Like all recycle systems, closed loop reverse osmosis is susceptible to buildup of impurities.

2. Solids in rinse water will "blind" the reverse osmosis membrane unless filtered out.

3. Current membranes have limited operating ranges for temperature, pH and chemical attack.

4. Maintenance costs and downtime tend to be excessive.

ION EXCHANGE

Description

Ion exchange is a well developed process which uses a packed bed of resin to selectively capture anions or cations from solution. The retention of specific ions results from the exchange of one ion from the surface of the solid resin particle for another in solution. A specific example is the two-step recovery of chromic acid from a rinse water.[17] The chromic acid is removed from rinse water by an ion exchange resin as follows:

$$H_2CrO_4 + 2HO{=}R \longrightarrow CrO_4{=}R + 2H_2O$$

Where: R=ion exchange resin.

After the resin is saturated with chromate, sodium hydroxide solution is used to regenerate the resin as follows:

$$2NaOH + CrO_4{=}R \longrightarrow Na_2CrO_4 + HO{=}R$$

The regenerated sodium chromate is passed through a cation exchanger to yield chromic acid suitable for reuse in the plating operation:

$$NA_2CO_4 + 2H{=}R \longrightarrow H_2CrO_4 + 2Na{=}R$$

The cation exchanger resin is regenerated with an acid such as hydrochloric:

$$2HCL + 2Na{=}R \longrightarrow 2H{=}R + 2NaCl$$

Ion exchange is a versatile, inexpensive technique which can be applied to many dilute metal bearing wastes in metal finishing. Most ion exchange operations are batch-wise processes going through the ion exchange and regeneration cycle consecutively. Continuous ion exchange units are available but are more capital intensive and complex to operate.

State-of-the-Art

Ion exchange technology is highly developed with general application installations numbering in the millions. Ion exchange has been used in electroplating applications for a number of years handling a variety of tasks. However, ion exchange is limited to dilute solutions since the resins are destroyed by excessive pH ranges.[17] In addition, cyanides are a problem since anion resins are readily poisoned by cyanide levels above 200mg/l.[17] EPA has funded a full-scale demonstration at the Singer Company, Elizabeth, New Jersey, to recycle cyanide, chromium and other toxic materials by ion exchange and ultra filtration. This project was funded for $29K and is scheduled to be completed in November 1976.

Economics

Capital expenditure for ion exchange would be expected to vary greatly since each system must be engineered for the particular application. Operating cost should be moderate, the regeneration chemicals being the major cost. Energy costs are low. A detailed economic study will be available from the EPA demonstration at the Singer Company in November 1976.

Advantages

1. Moderate capital and operating expenditures are required.
2. Recycle of chemicals can be practiced.
3. Sludge formation can be reduced by recycling.

Disadvantages

1. Ion exchange is applicable to dilute metal wastes only.
2. Resin beds are rapidly destroyed by strong oxidizing and reducing conditions.

ELECTRODIALYSIS

Description

Electrodialysis is a membrane cell process which can be applied to recover plating chemicals from rinse water. The electrodialysis cell consists of a series of compartments separated by alternating anion and cation permeable membranes (see Figure 6). A direct current is passed through the cell which causes the positive and negative ions to migrate through the membranes. The correct placing of the alternating membranes in relation to the electrical current flow causes the alternating cells to become more concentrated or less concentrated respectively. The cells are drawn off to produce deionized water for recycling and a concentrated solution. The concentrated chemical solution is returned to the plating tank and the deionized water is reused in the rinsing tanks.

In the closed loop configuration, chemicals are added to the plating bath to replenish the chemicals actually plated on the work pieces (or spilled). Water is added only to make up for spills and losses due to evaporation. As in any membrane process the key to successful operation is the membrane material.

A filter is used ahead of the cell to protect the membranes, although membrane blinding is not as serious in electrodialysis as in reverse osmosis. Impurity buildup in the system may be handled by ion exchange, chemical precipitation or activated carbon.

State-of-the-Art

Electrodialysis for rinse water recovery is in the early stages of demonstration on a full scale. The Industrial Waste Treatment Research Laboratory at Edison, New Jersey, has two grant programs in progress to demonstrate electrodialysis. One demonstration at the Keystone Lamp Manufacturing Corporation, Slatington, Pennsylvania, will use electrodialysis to recover cyanides from rinse water to produce zero discharge. This demonstration, funded at $15K, is scheduled for completion December 1975. The second demonstration, at the Risdon Manufacturing Company, Waterbury, Connecticut, will demonstrate electrodialysis recovery of nickel rinse water. The Risdon demonstration is funded at $25K and is scheduled for completion June 1976.

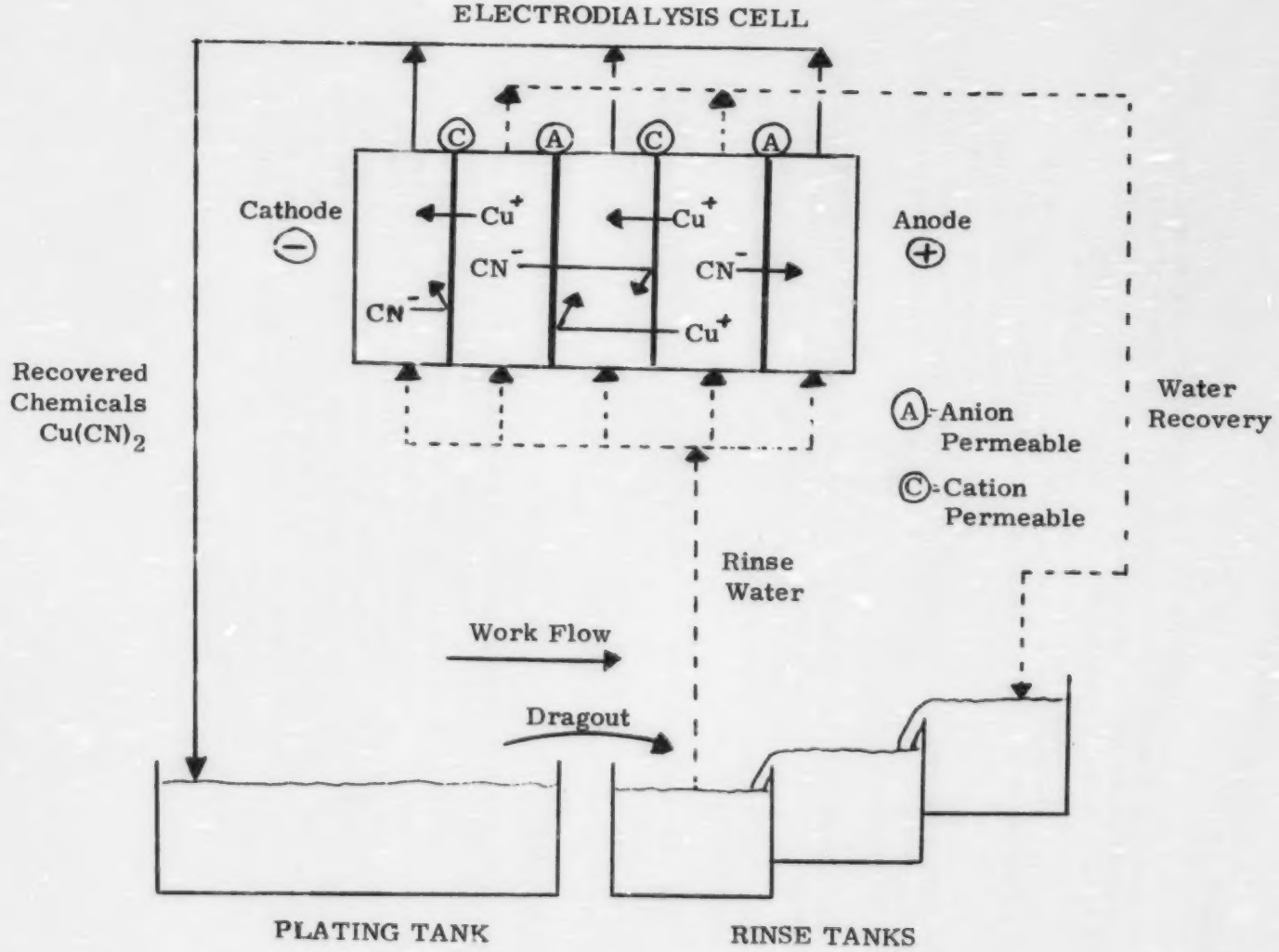


Figure 6 Closed-Loop Electrodialysis Recovery System

Economics

Full-scale operating costs and efficiencies are not available at this time. The two EPA funded demonstrations will develop economic and operating data.

Advantages

1. The plating chemicals in rinse water are recovered.

2. Sludge formation at wastewater treatment is reduced or eliminated.

3. Water usage is reduced in the rinsing operation.

Disadvantages

1. The closed loop system is susceptible to build-up of impurities.

2. Considerable electrical energy is consumed.

FREEZE SEPARATION

Principle

Freezing of wastewater to separate pure water and concentrate the dissolved waste is a technically feasible method of recycling dragout in rinse water. When water freezes, the solute is excluded from the ice crystal. When the ice is separated and remelted, relatively pure water is obtained. The remaining unfrozen solution becomes more concentrated due to the loss of water. A freezing unit would be required for each plating bath and rinse system analogous to an evaporation or reverse osmosis unit.

State-of-the-Art

Freezing technology is quite new and has not been applied to a full scale plating line. One manufacturer has reported successful completion of pilot-plant work on electroplating solution.[20] Full-scale applications of freeze separation have been limited to sea water desalinization.

Economics

Capital cost of current freeze separation units ($200 to $300K) is the major stumbling block to application for electroplating chemical recycling. Operating costs are also said to be significantly lower than evaporative separation due to lower energy consumption per pound of water separated.[20] Specific data on electroplating chemical recovery is lacking. However, unless the cost of freeze separation units becomes much lower, this technique will be of little interest to all but a few large electroplaters.

Advantages

1. The plating chemicals are recovered and recycled.
2. Heat sensitive plating solutions can be recycled.
3. Sludge formation at wastewater treatment is reduced or eliminated.
4. Water used for rinsing is reduced.
5. Energy operating costs are lower than for evaporative recovery.

Disadvantages

1. Current cost of freeze separation units is very high, discouraging all but very large plating operations.

2. The closed loop system is susceptible to buildup of impurities.

SOLVENT RINSING

Description

Solvent rinsing is a recycle technique which replaces the water in the first rinse after the plating bath with a water immiscible solvent. The dragged out water-plating chemical solution is removed from the work pieces with the solvent. The plating solution can then be phase separated from the solvent and returned to the plating bath. The solvent is returned to the rinse bath. In the second rinse, the solvent is rinsed from the parts with water and the water-solvent mixture is separated in a phase separator. The solvent phase is returned to the solvent rinse tank and the water is discharged to treatment. Figure 7 illustrates the process in diagram form.

State-of-the-Art

Solvent rinsing as a technique to recycle plating dragout is untried on a commercial scale. The key to the success of solvent rinsing is the selection of an appropriate solvent. Primary considerations for a solvent are:

1. Very low mutual solubility with water,
2. Chemical inertness,
3. Low surface tension to minimize emulsion formation, and
4. Flammability and toxicity.

The Industrial Waste Treatment Research Laboratory in Cincinnati has granted the Bumper Recycling Association of North America, Incorporated, $30K to study solvent rinsing using perchloroethylene. The pilot-plant study is being conducted in Cicero, Illinois. Completion of the study is expected in June 1976.

Economics

No economic data are currently available for solvent rinsing. However, the Bumper Recycling Association pilot-plant study with economic projections is expected after June 1976.

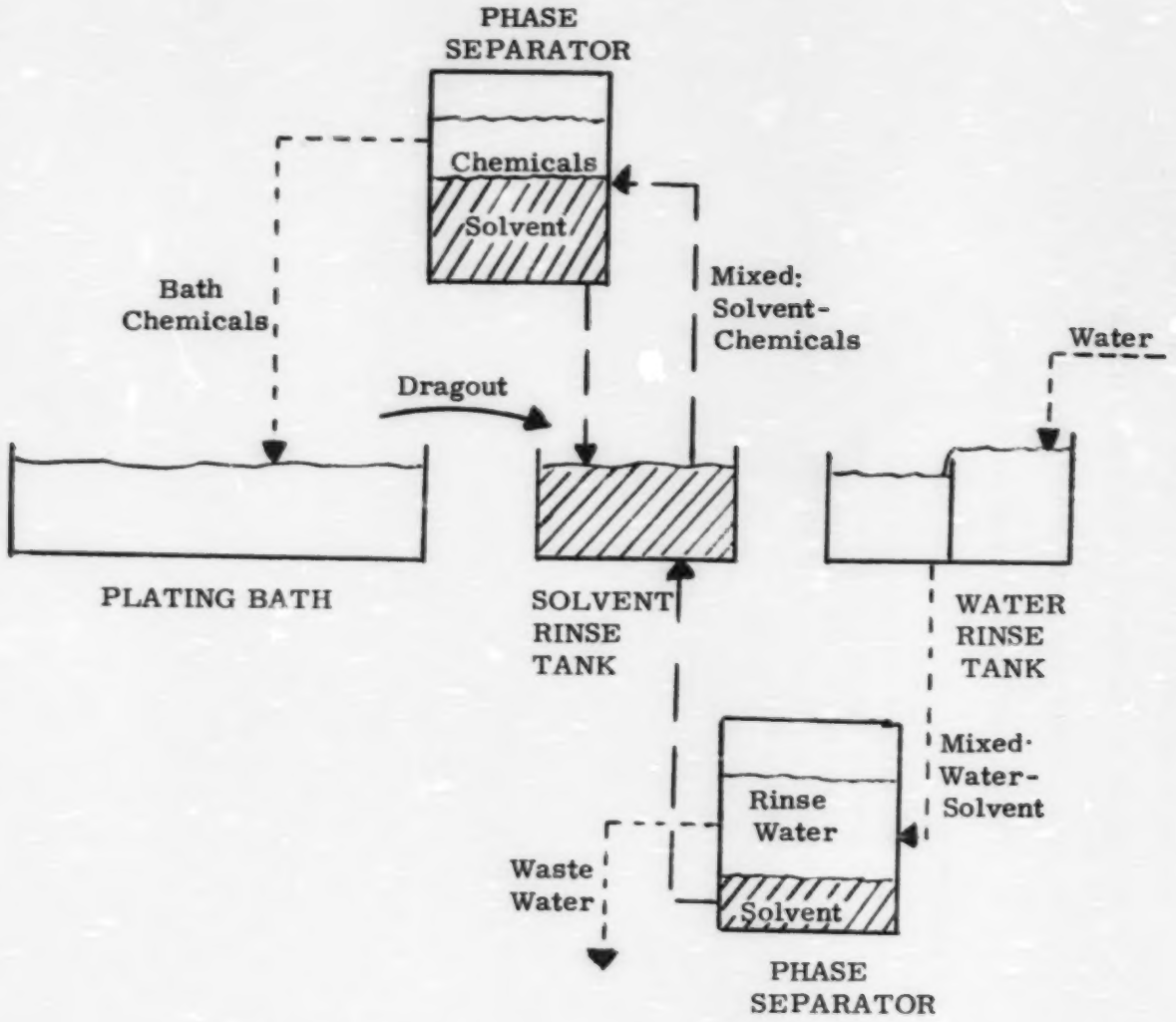


Figure 7 Solvent Rinsing System

Advantages (Anticipated)

1. Valuable chemicals are recycled.
2. Water use and waste treatment cost are reduced.
3. Sludge formation is reduced or eliminated.
4. The process does not involve complex technolgy.
5. The consumption of energy is minimal.

Disadvantages

1. Solvent contamination of the plating bath may cause product quality to deteriorate, depending on the solubility of the solvent in the plating solution and the efficiency of the liquid-liquid phase separation.

ION FLOTATION

Description

Ion flotation or foam flotation is a relatively well developed unit operation in the metal extraction industry. Application to electroplating wastewaters has not been demonstrated. The process uses a foaming agent and an inorganic ionic agent in water. An air pump called a foam generator injects the foaming and ionic agents with air into the bottom of a column filled with the solution to be extracted. A foam is generated in the column and the metal ions are captured by electrochemical forces in the foam. The foam is collected and removed on the liquid surface and the metal ions are recovered. A unique feature of this technique is that chromium may be recovered without reduction, and cyanides do not require destruction before treatment.[12] The foam is treated with caustic soda, soda ash or sodium silicate to break the foam and cause a separation. The separated metals are left concentrated in solution and can be recycled or recovered. The technique is anticipated to be simple, economical and effective for removal of pollutants at low concentrations in wastewater.

State-of-the-Art

Foam flotation for recovery and recycle of metals in solutions from electroplating operations is in the laboratory development phase. The Industrial Waste Treatment Laboratory, Edison, New Jersey, has granted $20K to Vanderbilt University, Nashville, Tennessee, to study electroplating waste recovery by foam flotation. This laboratory scale investigation was completed in December 1975. A final report is expected in April 1976.

Economics

No economic data for foam flotation of electroplating wastes are available. The laboratory study by Vanderbilt University will provide preliminary cost projections after December 1975.

Advantages

1. Foam flotation is expected to be a relatively low cost process for wastewater treatment and metals recovery.

2. The process may be potentially selective for certain metals.

3. The process has the potential for recovery and recycle of plating chemicals.

4. The potential for reduction or elimination of water treatment sludge is good.

Disadvantages

1. Foam flotation is an unproven technique for electroplating waste treatment.

D. External Recovery of Segregated Metals from Sludges and Solutions

Four processes or techniques to recover metal values from unmixed electroplating sludges and waste solutions are discussed. These processes/techniques are:

1. Integrated Treatment
2. Kastone Treatment Process
3. Single Metal Sludge Recovery
4. Spent Bath Recovery

INTEGRATED TREATMENT

Description

The integrated system treats the plating bath dragout at the source and allows segregation of individual metals as sludge. The treatment is accomplished by substituting a chemical precipitation bath in place of the first rinse after the plating bath. The dragout on the work piece is removed and reacted to form a sludge in the treatment tank. The treatment tank is circulated to a settling tank where the precipitate is allowed to settle and form a sludge.

The settling tank is also used as a make-up tank for addition of the treatment chemicals to maintain the system concentration. The treatment settling tank can be used for several plating lines which are plating the same metal, otherwise each plating bath requires a separate settling tank. Figure 8 illustrates the integrated system in block diagram. The integrated system offers a distinct advantage over "end of the line" conventional treatment because the metal sludges can be segregated and therefore offer much greater potential for recovery.

State-of-the-Art

The integrated treatment system is a fully developed technique and has received widespread applications. An EPA grant demonstration at Beaton and Corbin Company, a small captive shop, was published in 1973.[21] The Beaton and Corbin Company of Southington, Connecticut, installed integrated chemical treatment in its plant on two chromium lines, a copper cyanide bath and a nickel sulfate bath. An additional system was added to handle floor spills, acid rinse and alkali rinse baths. The effluent leaving the plant was upgraded to meet Connecticut discharge limits. The sludge formed from the four treatment systems was combined and pumped to drying beds before disposal. The prospects for sale and reclamation of segregated sludges from integrated treatment is unknown at this time.

Economics

The EPA demonstration at Beaton and Corbin yield the following cost data for the year 1970.[21]

Cost of installation	$47,337.00
Annual operating cost (including amortization)	$11,828.00
Treatment cost as percent of value added by the plating process	5.7%

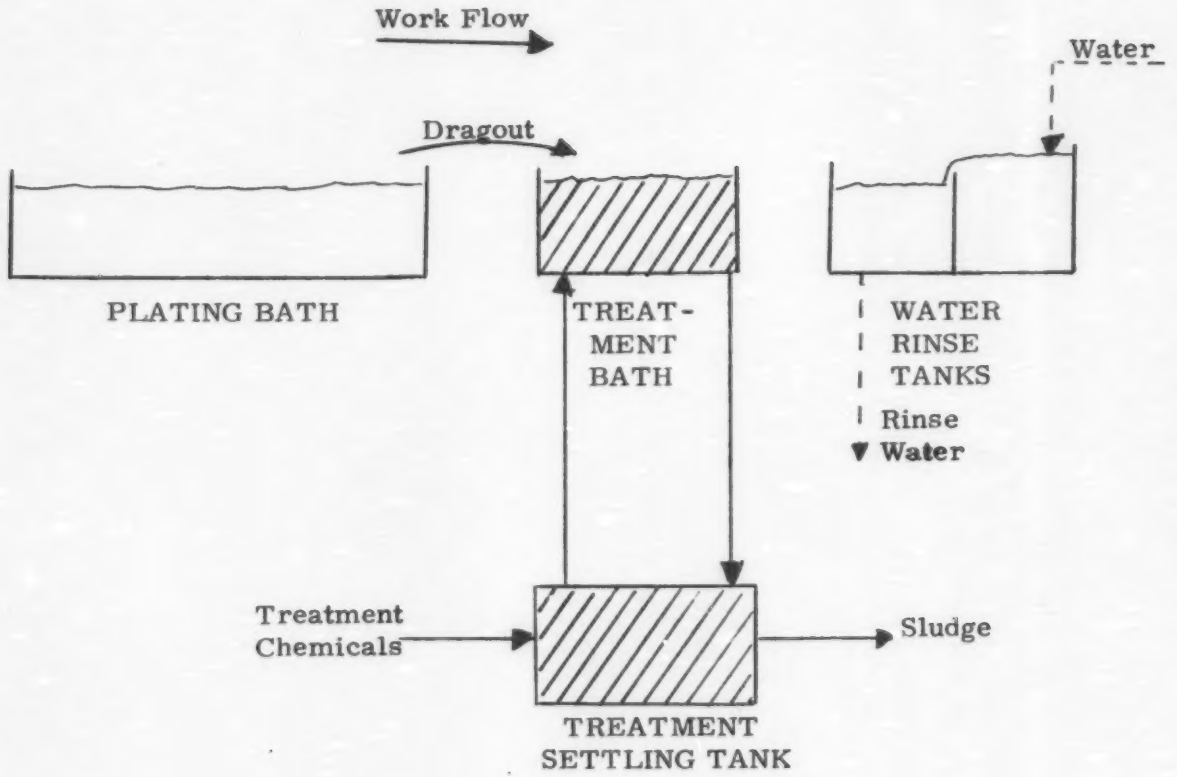


Figure 8 Integrated Waste Treatment System

The above economic data indicates that integrated treatment may well be within the cost capability of many small platers. A potential credit for metal recovery would offset part of the operating cost.

Advantages

1. Integrated treatment appears to be attractive to the small shop operator.

2. The operation of the treatment system is not complex and is within the capabilities of the small shop.

3. This technique appears to have good potential for recovery of metals since the metals are segregated in individual treatment systems.

Disadvantages

1. Feasibility of sale and recovery of the segregated metal sludges is not known.

2. If segregated sludges cannot be sold and/or recovered, this process offers little or no advantage over conventional treatment regarding land protection.

KASTONE® PROCESS

Description

A new process referred to as "Kastone," marketed by E.I. du Pont, Incorporated, Wilmington, Delaware, uses a proprietary peroxygen compound in the presence of formaldehyde to oxidize cyanide to cyanate in rinse waters from zinc or cadmium metal finishing operations. By treating wastewater with the proprietary solution, zinc and/or cadmium precipitates out as metal oxides. The precipitates are filtered. After treatment, the clarified water contains cyanate, ammonia and a glycolic acid amide. Since the cyanate ion is ten times less toxic than the cyanide ion, the treated effluent is normally discharged to a municipal sewer for further treatment. The process is finding some acceptance by small finishing shops.

The oxidized zinc and cadmium potentially may be recycled or reclaimed. The process to date is only applicable to zinc and cadmium cyanide solutions.

State-of-the-Art

The Kastone process is a full-scale treatment process being actively marketed by E.I. du Pont, Incorporated. The Industrial Waste Treatment Research Laboratory, EPA, Edison, New Jersey, has a $15K grant with Metal Plating Corporation, Connersville, Indiana, to demonstrate zinc cyanide removal and zinc oxide recycle. The zinc oxide precipitated is directly redissolved into the alkaline cyanide plating bath.[22] The final draft report from this demonstration is expected in November 1975.

Economics

Economic data for the Kastone process will be published in the Edison grant final report due in November 1975. Initial indications are that the process is competitive with other treatment technology.

Advantages

1. Zinc and cadmium sludge can be recycled to the plating bath.

2. The process is commercially available and reasonably priced.

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Disadvantages

1. Due to the presence of the toxic cyanate ion, the Kastone process will probably be limited to pre-treatment prior to discharge to municipal treatment systems.

2. The process is currently applicable to zinc and cadmium cyanide only.

SINGLE METAL SLUDGE RECOVERY

Description

Since metal recovery is relatively simple from a single metal sludge, rinse water from a single bath can be treated individually, as in the integrated system to produce a pure metal-containing sludge. One major electroplating supply company (OMI, Udylite, Detroit, Michigan) is recovering nickel from sludges produced at their customer's plants.[23] Nickel, which has a high value (approximately $3.00 per lb) is removed from nickel sulfate bath rinse water by precipitation with sodium bicarbonate as an insoluble nickel carbonate. The precipitate is settled and then dewatered by a filter press to 50 percent solids. The dry filter cake is shipped back to the supplier at one of four regional centers. The nickel carbonate is converted back to a high-grade nickel sulfate plating solution by a proprietary process. Pilot plant work to develop a similar copper recovery process is proceeding at Udylite.[28]

State-of-the-Art

Nickel recovery from nickel sulfate rinse waters is being practiced by a number of electroplating shops, such as General Motors, and Wald Manufacturing Company in Kentucky. OMI, Udylite, is handling the nickel sludge for recycle into high-grade nickel sulfide. Other metals may well lend themselves to this technique as their prices continue to increase.

Economics

The capital cost to the electroplating shop involves purchase and installation of a system to precipitate nickel in rinse waters and produce a 50 percent solids nickel carbonate sludge. This amounts to about $40K.[23] The sodium carbonate is purchased from the supplier/reclaimer. Shipping costs (the key to any regional recovery approach) are minimized by the high solids content obtained ($\approx$50%). The electroplater receives a credit against future nickel sulfate purchases based on the sludge shipment's weight and nickel assay. The credit reportedly averages 50 percent of the purchase price of new nickel sulfate baths. Reported recovery of nickel is about 95 percent for the complete process.

Advantages

1. This recycle technique potentially can handle many plating baths not amenable to direct recycling due to rapid breakdown of organic additives.

2. Sludge recovery is practical and economical for an external reprocessor operating on a regional basis.

3. Sludge generation in the wastewater treatment process is reduced.

Disadvantages

1. Probably not attractive to small shops due to capital requirements for each metal plated.

2. Economics depend on increasing metal prices and on a regional metal reprocessor.

SPENT BATH RECOVERY

Description

The periodic dumping of plating baths and stripping solutions is required to eliminate impurities dragged into the bath and thereby maintaining minimum quality standards. In many shops, the spent baths are bled into the wastewater at low enough rates to avoid upsets to treatment systems. Thus, these baths end up as sludge.

Due to the fact that spent baths are concentrated, compared to rinse waters, there is commercial interest by some waste processing firms in the recovery of metals from these unmixed baths.[24] [25] [26] Waste processors may be in a position to collect sufficient quantities of spent baths from a number of platers, so as to make recovery and sale of salvaged metals economically practical. The recovery of the metals from the spent baths may be accomplished by several processes. Conventional cyanide destruction followed by hydroxide precipitation may be practiced for cyanide baths. Ion exchange recovery may be practiced for a number of metal salts. In some cases, the bath chemicals are reacted to form saleable byproducts such as the process by Nieuwenhuis, U.S. Patent 3,443,328, which converts chromium waste solutions to lead chromate, which is sold as a paint pigment.[26]

State-of-the-Art

Several waste processors are reclaiming electroplating baths with varying degrees of success.[24] The market for the reclaimed metals or derivatives is the controlling factor in the profitability of this business.

Economics

The electroplater using a waste processor to dispose of his spent baths would require storage tanks to store sufficient quantities to justify a pickup. The waste processor would set his fee to produce a reasonable return on his investment. If the price of the recovered metals is high enough and the recovery process efficient enough, the cost to the electroplater might be reduced. Also, the reduction of the cost of waste treatment and sludge disposal would help offset the disposal fee.

Advantages

1. The technique is widely applicable to large and small shops due to minimal capital investment required.

2. Sludge from spent bath treatment would be eliminated.

3. Metals can be reclaimed for reuse.

Disadvantages

1. Some investment in storage tanks to hold spent baths before pickup is required.

E. Recovery of Metals From Mixed Hydroxide Sludges

Two types of potential processes have been identified as having the potential to recover metals from hydroxide wastewater treatment sludges. These are:

1. Solvent Extraction

2. Electrochemical and Roasting

SOLVENT EXTRACTION

Description

A potential process technique for recovery of metals from hydroxide sludges is solvent extraction. The process depends on organic reagents which are selective for specific metals. The basic process involves leaching of the sludge to solubilize the metals. The leach liquor is contacted with an organic solvent containing a selective reagent. The reagent extracts a specific metal ion. The organic phase is then separated and treated further to recover the metal.

State-of-the-Art

Solvent extraction of metal containing sludge is currently in the laboratory state of development. In the United States, EPA has funded a grant for $80K to Texas Southern University to develop a solvent extraction process. The project is being monitored from the Industrial Waste Treatment Research Laboratory at Edison, New Jersey, and completion is expected in May 1976.

A Swedish firm, MX Processer in Gotenborg, has announced a process developed by their company which will recover metals from electroplating sludges.[27] The process, named MAR for "Metals and Acid Recovery," recovers copper, zinc and nickel for sale. HWMD has been in contact with the inventor, Dr. Reinhardt of MX Processers, to obtain additional information. However, patent considerations preclude release of information by MX Processers at this time.[28]

Economics

The initial prototype MAR process is expected to break even economically assuming hydroxide sludges are delivered to the plant free of cost.[27] No other information on potential economics is known at this time. The Texas Southern University grant report, due May 1976, will contain some economic projections.

Advantages

1. The recovery of metals from the sludge reduces the hazard of disposal.

2. The metals are recovered for recycle.

3. The economics of the process may be favorable.

4. Energy usage is expected to be low.

Disadvantages

1. Although the sludge can be detoxified, disposal of a residual sludge will still be required.

METAL RECOVERY - ELECTROCHEMICAL AND ROASTING

Description

Another proposed approach to recover the metals from electroplating sludges and metal bearing solutions is the use of electrolysis and high temperature roasting techniques. In this recovery approach, the sludge is leached with a strong reducing agent such as ammonium carbonate or sulfuric acid to solubilize the metal hydroxides. The leach liquor is then subjected to controlled potential electrolysis to remove copper. A roasting technique separates chromium and zinc. A detailed process description is not possible due to the preliminary state of development.

State-of-the-Art

Work on this approach to recovery of metals from sludges and waste solutions is still in the laboratory stage. The Bureau of Mines, Rolla Metallurgy Research Center, is conducting active experimental work into process approaches for metals recovery.[29]

Battelle-Columbus Laboratories is developing a process to recover metal values from water treatment sludge under a $104K EPA grant from the Industrial Waste Treatment Laboratory, Edison, New Jersey. The current study started July 1975, following a preliminary study completed April 1975. Battelle plans to build a small pilot plant which will be portable, for on-site evaluations.[30] The project is expected to be completed by July 1976.

Economics

Economics are uncertain. The evaluation report from Battelle-Columbus Laboratories indicated unfavorable economics.[31] Operating costs for a plant processing five tons per day (dry basis) of sludge were estimated at $1,740 per day. The recovered metals could be sold for $640 per day leaving a cost deficit of $1,090 per day. The current study, expected to be completed by July 1976, should give more accurate projections of operating and capital costs for the Battelle process.

Advantages

1. The sludge will be detoxified, eliminating the environmental hazard arising from land disposal.

2. The metal values can be recovered for sale.

Disadvantages

1. A detoxified sludge will still require disposal.
2. Present economic projections are not favorable.

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